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Microcolumn-based speciation analysis of thallium in soil and green cabbage

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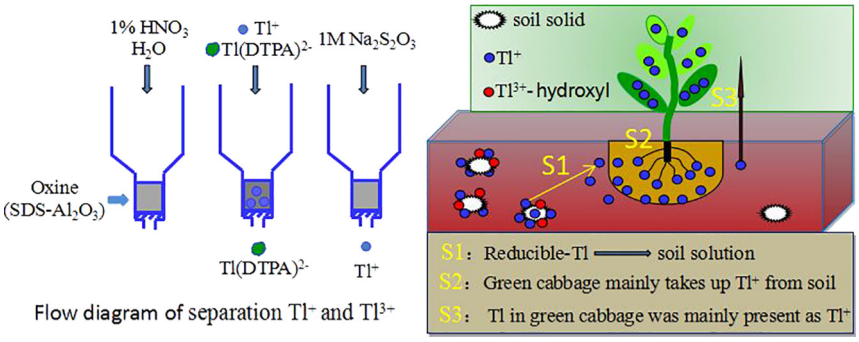
HIGHLIGHTS

- An efficient method separating and detecting Tl species for soil and plant samples was elaborated.
- Tl in green cabbage was mainly present as Tl(I).
- Green cabbage mainly takes up Tl (I) from soil.
- The reducible fraction was the main carrier for Tl in soil.

GRAPHICAL ABSTRACT



Flow diagram of separation Tl^{+} and Tl^{3+}

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ABSTRACT

Thallium (Tl) is a toxic trace metal, whose geochemical behavior and biological effects are closely controlled by its chemical speciation in the environment. However, little tends to be known about this speciation of Tl in soil and plant systems that directly affect the safety of food supplies. In this context, the objective of the present study was to elaborate an efficient method to separate and detect Tl(I) and Tl(III) species for soil and plant samples. This method involves the selective adsorption of Tl(I) on microcolumns filled with immobilized oxine, in the presence of DTPA (diethylenetriaminepentaacetic acid), followed by DTPA-enhanced ultrasonic and heating-induced extraction, coupled with ICP-MS detection. The method was characterized by a LOD of 0.037 μg/L for Tl(I) and 0.18 μg/L for Tl(III) in 10 mL samples. With this method, a second objective of the research was to assess the speciation of Tl in pot and field soils and in green cabbage crops. Experimental results suggest that DTPA extracted Tl was mainly present as Tl(I) in soils (>95%). Tl in hyperaccumulator plant green cabbage was also mainly present as Tl(I) (>90%). With respect to Tl uptake in plants, this study provides direct evidence that green cabbage mainly takes up Tl(I) from soil, and transports it into the aboveground organs. In soils, Tl(III) is reduced to Tl(I) even at the surface where the chemical environment promotes oxidation. This observation is conducive to understanding the mechanisms of Tl isotope fractionation in the soil-plant system. Based on geochemical fraction studies, the reducible fraction was the main source of Tl getting accumulated by plants. These results indicate that the improved analytical method presented in this study offers an economical, simple, fast, and sensitive approach for the separation of Tl species present in soils at trace levels.

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1. Introduction

Thallium (Tl) is a nonessential trace metal. It is more toxic to mammals than cadmium, lead and even mercury (Nriagu, 1998), and is therefore categorized by many countries and international agencies as one of 13 priority metal pollutants (Keith and Telliard, 1979). Worldwide, the Tl content of soils seems to depend largely on the geological origin of the parent material (Sager, 1998; Jacobson et al., 2005). Some soils have a naturally high background concentration of Tl, like the clayey soils developed on the Sinemurian limestone in France, with natural Tl contents as high as 55 mg/kg (Tremel et al., 1997; Escarre et al., 2011; Resongles et al., 2014), but in general, Tl concentrations in uncontaminated surface soils range from 0.1 to 2 mg/kg, with most reported concentrations <1 mg/kg (Fergusson, 1990; Heim et al., 2002). In anthropogenically-contaminated soils, Tl concentrations can vary substantially, as high in some cases as, e.g., 15 mg/kg in soils near cement factories in Germany, 61 mg/kg in mine tailings-impacted soils in China, 73 mg/kg in soils near old mines in Germany (Sholl, 1980; Zhou and Liu, 1985), 8.8–27.8 mg/kg in soils from Silesian–Craeowian zinc–lead mine areas in Poland (Lis et al., 2003), and 3.0–27.6 mg/kg in soils from abandoned Pb-Zn-Cu mining area in Turkey (Sasmaz et al., 2007).

Such high concentrations of Tl, in soils that may be used for the production of food crops, cause serious concerns in terms of food safety. Indeed, when grown on Tl-contaminated soils, certain crops take up high levels of Tl (Xiao et al., 2004; Pavlickova et al., 2006; Vanek et al., 2010). For instance, *Brassica oleracea* L. *var. capitata* L. (green cabbage) accumulates large amounts of Tl (LaCoste et al., 2001; Al-Najar et al., 2005; Pavlickova et al., 2005).

In terms of potential toxicity, the form that Tl has in these crops is not irrelevant. Indeed, of the two oxidation states, monovalent Tl(I) and trivalent Tl(III), that Tl can have in soils or plants, the trivalent form, Tl(III), is out to be approximately 50,000 times more toxic than Tl(I) on a free-ion basis (Ralph and Twiss, 2002). Because of this large difference in toxicity between the two forms of Tl, a thorough understanding of the redox transformations of Tl and of its fate in soils and crops is required in order to evaluate the potential risks associated with the uptake of Tl by crops. Some research has been carried out on the subject in the last few years (Al-Najar et al., 2003, 2005; Xiao et al., 2004), and several aspects of the topic have been elucidated. Tl(I) shows both chalcophile and lithophile character, i.e., small amounts of Tl(I) are often found in metal sulfides, and Tl(I) readily substitutes K^+ in minerals such as K-feldspars or micas due to its similar ionic radius (Lin and Nriagu, 1998). Tl(I) is relatively soluble, mobile and bioavailable, similar to alkali metal cations. In aquatic environment at low Tl concentrations, Tl(I) tends to dominate over Tl(III), due to the high redox potential of Tl(III)/Tl(I) couple (Eh = 1.28 V) and mostly in the form of hydrated Tl^+ due to limited complexation (Casiot et al., 2011). However, photochemically driven reactions to sunlit surface waters or microbiological processes may lead to Tl(I) oxidation (Twining et al., 2003; Karlsson et al., 2006), and Tl(III) may be stabilized by hydrolysis and colloid formation or sorption to Fe(III)-colloids (Lin and Nriagu, 1999; Karlsson et al., 2006). In contact with certain Mn(IV)-oxides, Tl(I) can be oxidized to Tl(III)-complexes and stabilized by incorporation into Mn(IV)-oxide (Peacock and Moon, 2012).

Unlike with some of the other trace metals found in terrestrial environments, information about what controls the redox chemistry of Tl in any given soil, or in plants that grow on it, remains very scanty (Al-Najar et al., 2003, 2005; Xiao et al., 2004). As a result, it is not possible at the moment to predict quantitatively what the chemical speciation of Tl is in soils at specific locations, and therefore to assess satisfactorily what risk may be associated with growing crops (in particular cabbage) on these soils.

Chemical speciation of Tl can be determined directly by chromatographic separation followed by elemental detection, usually with ICP-MS, ICP-OES, ICP-AES, GFAAS or ETAAS (Lin and Nriagu, 1999; Hu, 2002; Coetzee et al., 2003; Nolan et al., 2004; Meeravali and Jiang, 2008; Krasnodebska-Ostrega et al., 2008, 2012; Casiot et al., 2011). Most of those methods needed ion exchange resin chromatography to separate Tl(I) and Tl(III) with high cost (Lin and Nriagu, 1999; Nolan et al., 2004; Casiot et al., 2011). Dadfarnia et al. (2007) proposed a procedure based on the use of microcolumns of immobilized oxine in order to pre-concentrate and separate the different forms of Tl. In this method, in the presence of EDTA, only Tl(I) is retained in the microcolumn, leading to the successful separation of Tl(I) and Tl(III) in solution. The preparation of the microcolumns themselves is straight forward and economical. However, both Tl(I) and Tl(III) can form complexes with EDTA ($\log K_{Tl(I)\text{-}EDTA} = 5.3$, $\log K_{Tl(III)\text{-}EDTA} = 22.5$) (Lin and Nriagu, 1998), this lowers the separation efficiency. In addition, the presence of organic substances in complex matrix samples may also influence the separation efficiency, especially for soil and plant matrices. For example, humic acid complex with Tl(III) has a similar stability constant with EDTA (Bidoglio et al., 1997). Compared to EDTA, more stable complexes are formed by Tl(III) with DTPA ($\log K = 46$), whereas Tl(I) cannot be complexed at all by DTPA (Inczedy, 1976; Lin and Nriagu, 1998). Therefore, use of DTPA as the chelant can help improve the separation efficiency and stabilize Tl(III) (Biaduń et al., 2016; Sadowska et al., 2016).

For the determination of Tl speciation in solid samples (plant, soil, etc.) to have maximum efficiency (Sadowska et al., 2016), the extraction of Tl(I) and Tl(III) from the sample matrix should be carried out in such a way that the original speciation remains unaltered. For the determination of total Tl from solid environmental samples, nitric acid, hydrofluoric acid or chloroacetic acid are usually used as extracting agents. However, they cannot be used to prepare samples for Tl species analysis, because they tend to change the original speciation of Tl in samples. In earlier laboratory Jia (2013) found that 28% and 100% of Tl (I) would be oxidized to Tl(III) by nitric acid and chloroazotic acid, respectively, so that only neutral extraction agents should be considered for Tl species extraction from solid samples. However, the extraction efficiency in this case is low (Jia, 2013). Some complementary techniques are often used to improve the chemical extraction efficiency. For example, ultrasonic extraction for solid samples can significantly improve metal extraction efficiency, and is preferred in the context of element speciation (Marin et al., 2001).

In this general context, the first objective of the research described in the present study was to devise a microcolumn-based method and DTPA as the chelant to determine quantitatively the concentration of Tl(I) and Tl(III) in soil and plant samples. A new extraction technology with ultrasonic was also developed for extraction Tl(I) and Tl(III) from soil and plant samples. This method was then used to determine the chemical speciation of Tl in Tl-rich soil and green cabbage samples to better understand redox transformations of Tl in the soil-plant system.

2. Method and materials

2.1. Microcolumn separation of Tl(I) and Tl(III)

2.1.1. Preparation of the sorbent and microcolumn

Fifty milliliters of a solution (pH ≈ 5) containing 100 mg SDS (Sodium dodecyl sulfate) was added to 1.5 g of alumina (10–50 μm, γ-type chromatography grade). The solution was mixed with a magnetic stirrer for 10 min. The supernatant was decanted and the SDS-coated alumina was washed thoroughly with several portion of water. Then ~20 mL of water and 5–7 mL of oxine solution (0.1 g dissolved in acetone) were added. The solution was shaken for 15 min. The mixture was then filtered through Millipore filter, washed, air-dried and was kept in close bottle before use (Dadfarnia et al., 2007).

A microcolumn made of a 4 cm-long PTFE tube (BIO-RAD, USA) with a 6 mm inner diameter was used. The microcolumn was full of oxine immobilized in surfactant-coated alumina (~400 mg). The tube bottom was fitted with foam to retain the sorbent.

2.1.2. Procedure

The microcolumn was cleaned and pre-equilibrated with ultra-pure water and 1% HNO_3. Before flowing into the microcolumn, the pH of extracted solutions was adjusted to 6–7 using 0.01 M ammonium hydroxide ($NH_3 \cdot H_2O$). The flow of extracted sample solution into the microcolumn was controlled at 2.0 mL/min by a peristaltic pump. Tl(I) and Tl(III) present as free Tl(I) ions and Tl(III)$DTPA^{2-}$ complex, respectively in the digested sample solution when the presence of a certain concentration of DTPA (see Section 2.2). When the digested sample solution across the microcolumn, only Tl(I) ions is adsorbed onto the sorbent. After the sample had passed through the microcolumn, 2 mL of a 1 M sodium thiosulfate was injected to flush the Tl(I) which adsorbed onto the microcolumn. All washings and elutions were collected, respectively for measurement Tl(I) and Tl(III).

2.1.3. Selectivity

To test the selective nature of the method, when more than one species is present in a sample, nine mixed inorganic standards containing different levels of Tl(I) and Tl(III) were prepared by diluting the stock solutions and three replicates were processed to ascertain the recovery rates.

2.1.4. Breakthrough test

One liter of 500 μg/L and 10 μg/L Tl(I) standard solution contains 5 m mol/L DTPA and the pH was adjusted to 6–7 using 0.01 M ammonium hydroxide was passed through a microcolumn containing 400 mg of adsorbent, respectively. The eluted liquid phase was collected every 100 mL for Tl(I) determination by ICP MS. The significance was defined by $Ce/C_0 < 5\%$ (Ce/C_0 = Tl in elution/Tl in original solution) (Lin, 1997).

2.1.5. Stability of Tl(III) solutions with DTPA

Tl(I) is stable in aqueous solution, whereas Tl(III) is reactive, can be hydrolysed and reduced in alkaline and neutral solutions, and can be reduced by common reducing agents. The present study used DTPA to stabilize Tl(III), as follows. A 0.2 mL volume of supersaturated bromine water (5 wt%) was added into the concentrated Tl^{3+} solution (20 mL 100 μg/L for Experiment A and B, 50 mL 100 μg/L for Experiment C) and was mixed thoroughly for 5 min to ensure that Tl was present solely as Tl^{3+} in solution, as indicated when the solution went from colorless to orange. Subsequently, three separate procedures were carried out. (1) Experiment A: the solution was held at 60 °C on an electric heating plate. Heating was continued. After 0, 5, 10, 20 and 30 min, respectively, 20 mL of 5 mM DTPA were added each time to the solution, and the concentration of Tl(I) and Tl(III) was assayed. (2) Experiment B: 20 mL 5 mM DTPA was added to the solution, followed by thorough mixing for 5 min. The solution was then heated to 60 °C on an electric heating plate, after which the solution went back from orange to colorless. Under continuous heating, the concentration of Tl(I) and Tl(III) was assayed after 0, 5, 10, 20 and 30 min, respectively. (3) Experiment C: 50 mL 10 mM DTPA was added to the solution, followed by thorough mixing for 5 min. The solution was then ultrasonically (at 4 kHz) and by heating (at 60 °C) in a mechanical, after which the solution went back from orange to colorless. Under continuous heating and ultrasonically, the concentration of Tl(I) and Tl(III) was assayed after 0, 10, 30, 60, 120, 240, 480 and 720 min, respectively. Each treatment was replicated three times.

2.1.6. Reagents, solutions and standards

All the chemicals as well as solvents used in the experiments were reagent grade, used without further purification, except for nitric acid which was of ultrapure grade. Ultra-purewater (18.2 MΩ cm) was obtained from an Milli-Q50 system (Millipore, and France). A stock solution (1000 mg/L) of Tl(I) and Tl(III) was prepared by dissolving an accurate weight of either $TlNO_3$ (Merck, Germany) or $Tl(NO_3)_3 \cdot 3H_2O$ (Merck, Germany) into a 100 mL flask, and diluting it to the mark with 1% HNO_3. A supply of the stock solution was prepared daily by serial dilution with ultra-pure water. A sodium thiosulfate solution (1 M) was prepared by dissolution of 25.06 g of $Na_2S_2O_3 \cdot 5H_2O$ into a 100 mL flask and diluting to the mark with ultra-pure water. A 0.1% solution of oxine (i.e., 8-hydroxyquinoline) was prepared by dissolving 100 mg of oxine in acetone. DTPA solution (5 mM) was prepared by dissolution of 1.9668 g of DTPA into a 1000 mL flask and diluting to the mark with ultra-pure water.

2.2. Preparation of plant and soil samples

2.2.1. Preparation of plant samples

Plant samples were collected from both Tl-polluted field and pot experiments. For the pot experiments, soil was collected from a forest land, in the suburbs of Guiyang, China. Soil samples were air-dried and passed through a 2 mm diameter sieve. Tl was artificially mixed with each soil sample, as Tl^+ (12 mg/kg, TlCl) and Tl^{3+} (8 mg/kg, $Tl(NO_3)_3 \cdot 3H_2O$). After undergoing three cycles (15 d per cycle) of saturation with deionized water (made Tl fraction distribution achieve a relative balance) and air-drying, 2.5 kg soils with different Tl amounts were placed in plastic pots (25 cm height, 20 cm diameter), and each treatment was replicated three times. Seeds of green cabbage were purchased from the Vegetable Research Institute of Guizhou Agricultural Academy. After being superficially sterilized in 0.5% sodium hypochlorite (NaOCl) and rinsed thoroughly with deionized water, seeds were sowed with the feeding block of the man-made climate box (RXZ-300C-type). After about 5 d, plants with uniform size were transplanted to each pot (one plant one pot). After one week, Ca^{2+} ($Ca(NO_3)_2 \cdot 4H_2O$) was added to the soils five times to obtain a Ca concentration of 3.0 g/kg. Plants were grown for 12 weeks in a controlled-environment growth chamber (temperature of 25–30 °C, humidity of 40–60%). Tap water was provided to the pots every day to maintain a moisture level just below field water capacity to avoid the release of leachate from the pots. Fertilization of the pot was performed approximately every one week, using 0.1 L 50% Hoagland Solution (Hoagland and Arnon, 1950) without $Ca(NO_3)_2 \cdot 4H_2O$ for each pot. After this growth period, green cabbage samples were harvested and separated into root, stem and leaf. Roots were thoroughly washed using deionized water to eliminate adhering soil particles. Roots, stems and leaves were either used immediately after harvesting for species analysis or quickly freeze-dried for future analysis.

Green cabbage samples (B102, B203 and B204) were collected from the Tl-polluted area of Lanmuchang, a rural area in southwest Guizhou Province, China (Jia et al., 2013). The plant samples were treated like those of harvested pot plants.

2.2.2. Preparation of soil samples

The pot soil before plant and rhizospheric soil after planted samples were collected and quickly freeze-dried for future analysis. The soils were processed for geochemical analysis by disaggregation to pass through a 2-mm sieve. The sieved fractions were then ground in a Bico ceramic disc grinder followed by reduction to 80-mesh (<180 μm) powder in a ceramic ball mill.

In the Tl-polluted field, at each plant sampling site, the rhizospheric soils (S102, S203 and S204) were also collected, respectively. The soil samples were treated like those of pot soils.

2.2.3. Sample extract for Tl species analysis

All samples were transported back to the laboratory immediately after sampling and processed within 8 h of collection. Samples of 1000 mg of the soil (freeze-dried) and 500 mg of the plant materials (wet weight, roots, stems, young leaves and old leaves) were placed into100-mL round-bottom, covered centrifuge tubes. To each tube, 50 mL of a 5 m M DTPA solution was added. A stopper was added. Extraction was carried out ultrasonically (at 4 kHz) and by heating(at 60 °C) in a mechanical shaker for 4 h, and then each tube was centrifuged (at 3000 g for 10 min). The liquid was decanted, and this step was repeated

a second time. The extracted solution was mixed and filtered through 0.45 μm Millipore membranes. Tl in the extract occurs in two chemical forms: free Tl(I) ions and Tl(III)DTPA complex. Before species analysis, the pH of extracted solutions was adjusted to 6–7 using 0.01 M $NH_3 \cdot H_2O$.

2.3. Sequential extraction of soil

The full protocol for the sequential extraction of Tl in soil samples, i.e., the separation of Tl into water soluble, weak acid soluble, reducible, oxidizable, and residual fractions (Table 1), was performed in accordance with the modified BCR procedure (Rauret et al., 1999). To evaluate the intensity of experimental contamination, blank experiments were performed under the same conditions, and the results suggested that no significant Tl contamination was introduced into the sequential extraction. The recovery of Tl was determined by comparing the amount of Tl extracted from the total amount indicated by its total digestion concentration: (sum/total) × 100%. In this study, the recovery rate of Tl was within the range of 102–116%.

2.4. Analysis and quality control

The soil pH was measured after suspending soil in de-ionized water in a ration of 1:2.5 mass/volume using a pH meter (AISI pHB9901, Taiwan). The concentration of soil organic material (SOM) was determined by catalytic oxidation (1350 °C) using a combination of Metalyt CS 500 and Metalyt CS 530 elemental analyzers (Eltra, Germany). The cation exchange capacity (CEC) of the soil was computed after saturation of the soil samples with 0.005 M EDTA, 1 M ammonium acetate mixture, followed by titration with ammonia acid. 1 mol/L sodium acetate as exchange extractant was acted with Ca^{2+} in soil and the exchangeable Ca^{2+} in the solution was measured with the inductively coupled plasma spectrometer [(ICP-OES) iCAP 6500, Thermo Scientific, Germany] after filtration.

Approximately 50 mg of sieved soil sample (<180 μm) was digested using a heated acid mixture (15 mL of 15 M HNO_3 and 5 mL of 10 M HF) to determine the concentration of total Tl. Additionally, 100 mg of powdered plant samples was digested with a 10 mL mixture of strong acids (8 mL of 15 M HNO_3 and 2 mL of 10 M HF) for total Tl determination.

All the analytical measurements of Tl in the different contexts were performed via ICP-MS (Perkin-Elmer, ELAN DRC-e, USA) by standard addition with Rh (10 μg/L) as an internal standard. The limit of detection (LOD) for Tl species analysis was calculated as a mean value increased by 3-times the standard deviation of Tl concentration in the blank sample (10 mL) ($x + 3$ SD, n = 10) and it amounts to 0.037 μg/L for Tl(I) and 0.18 μg/L for Tl(III), respectively. The detection limit of total Tl for soil and plant samples was 0.01 mg/kg. The analytical precision, determined on the basis of the standard quality control procedures using internationally-certified reference materials (OU-6, AMH-1, GBPG-1, NIST 2711 and GBW07405), duplicates, and reagent blanks, was better than ±10%. The data relative to plants are reported as dry weight (DW).

Table 1
Reagents and operation conditions for modified BCR sequential extraction procedure (Rauret et al., 1999).

Step	Operationally-defined phase	Reagent	Stirring time and temperature
1	Water soluble[a]	30 mL of H_2O	1 h at 22 ± 5 °C
2	Weak acid soluble[b]	40 mL of 0.11 M HOAc	16 h at 22 ± 5 °C
3	Reducible[b]	40 mL of 0.5 M $NH_2OH \cdot HCl$	16 h at 22 ± 5 °C
4	Oxidizable[b]	10 mL of 8.8 M H_2O_2	1 h at 22 ± 5 °C
		10 mL of 8.8 M H_2O_2	1 h at 85 ± 5 °C
		50 mL of 1 M NH_4Ac	16 h at 22 ± 5 °C
5	Residual[c]	HNO_3 + HF	As described in Section 2.4

[a] Jakubowska et al., 2007.
[b] Rauret et al., 1999.
[c] Qi et al., 2000.

Table 2
Determination of Tl species in synthetic solution. Data are presented as mean ± SD (n = 3).

Contents Tl(I) + Tl(III) (μg/L)	Recovery rate (%)[a]	
	Tl(I)	Tl(III)
10.0 + 0	96.8 ± 3.1	–[b]
50.0 + 0	98.8 ± 2.2	0.39 ± 0.04[c]
100 + 0	98.5 ± 4.5	0.57 ± 0.08[c]
0 + 10.0	0.20 ± 0.06[c]	104 ± 2.0
0 + 50.0	0.46 ± 0.07[c]	97.7 ± 2.2
0 + 100.0	1.30 ± 0.11[c]	98.9 ± 4.7
10.0 + 100	98.3 ± 4.0	97.6 ± 1.3
50.0 + 50.	102 ± 2.4	98.2 ± 0.8
100.0 + 10.0	98.1 ± 1.9	106 ± 0.7

[a] Mean and S.D. of three independent measurements.
[b] Less than LOD.
[c] The detection value (mean ± SD, n = 3, μg/L).

3. Results and discussion

3.1. Extraction and separation of Tl(I) and Tl(III)

Results obtained with the method of improved from Dadfarnia et al. (2007), in the presence of DTPA, indicate only Tl(I) was retained on the column. The results (Table 2) showed good recoveries for both Tl(I) and Tl(III), indicating that the microcolumn system was able to discriminate accurately among the different forms of Tl. The breakthrough test results showed insignificant Tl(I) detection during the eluting process, and all the $Ce/C_0 < 2\%$. The breakthrough capacity of immobilized oxine microcolumn under the working conditions exceeded 1000 μg of Tl(I) per gram of packing materials. This high value suggested high performance of microcolumn even in the presence of competing ions.

Tl(III) is less stable and can be electrochemically reduced to Tl(I) very fast ($\log K \cong 40$, $E_{red}(Tl^{3+}/Tl^{+}) = +1.26$ V). The reduction is faster than complexation of Tl(III) (Biaduń et al., 2016). In this study, a second series of experiments attempted to assess the effect of DTPA on the stabilization of Tl(III). The experimental results (Figs. 1, 2) strengthens the evidence of the former theoretical analyses and show that in the absence of DTPA, about 40% of Tl(III) was reduced to Tl(I) after heating for 30 min. On the contrary, in the presence of DTPA, the reduction of Tl(III) to Tl(I) was virtually absent.

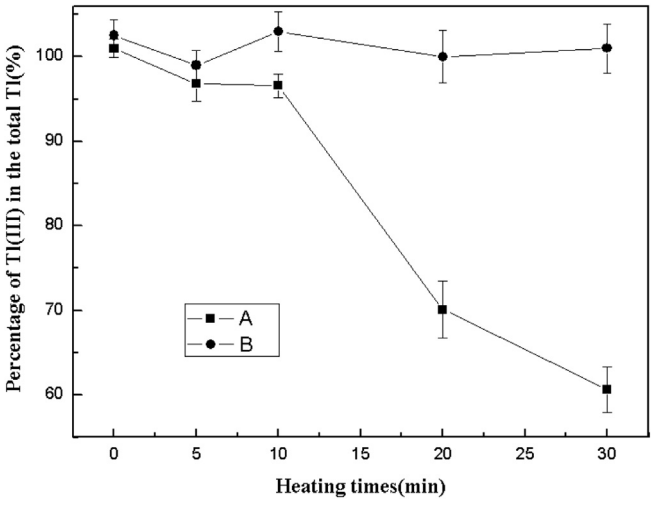

Fig. 1. Stabilization of Tl(III) in solution as a function of heating time after an initial addition of DTPA (Experiment A) or when DTPA is absent every 5 min (Experiment B). Data are presented as mean ± SD (n = 3).

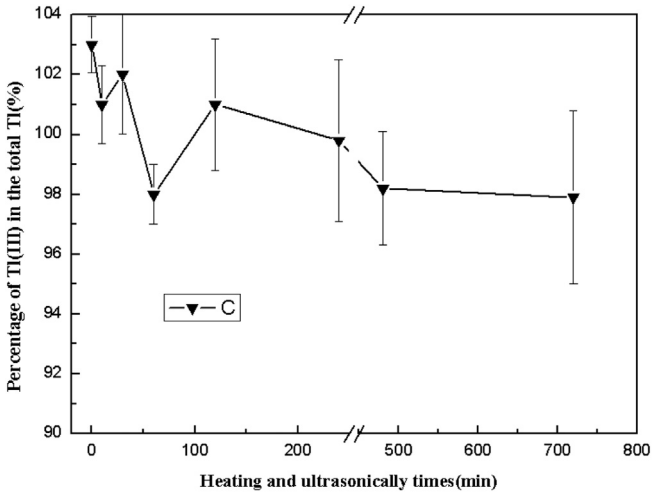

Fig. 2. Stabilization of Tl(III) in solution as a function of heating and ultrasonically time after an initial addition of DTPA (Experiment C). Data are presented as mean ± SD (n = 3).

The extraction rate is summarized in Tables 4 and 5. The results show that high extraction rates are reachable for green cabbage samples, i.e., 91.7–101% for roots, 92.9–112% for stems, 90–108% for young leaves, and 95–104% for old leaves, respectively. In the case of soil samples, the extraction rate was low, ranging from 3.2 to 11.3%, particularly for pot soils after vegetation had grown. Nevertheless, the DTPA-extracted Tl content from soil is higher than that in the bioavailable fraction (i.e., water soluble and weak acid soluble) of sequential extraction (Fig. 3), and can be considered as the maximum mobile Tl (easily access to soil solution) in the surface environment. Thus, we propose that Tl in the DTPA-extracted fraction in soil has a linkage to Tl species uptake by crop plants.

3.2. Tl speciation in soil and green cabbage

Analysis of the soils indicates that they are acidic with generally low pH (5.4–6.3). The soil organic matter (SOM) contents in soils vary from 63.0 to 146 g/kg, and low SOM contents corresponded to high CEC (Cation exchange capacity) values (Table 3). The results for the sequential extraction of the soil samples (Table 4) show that in the field soil, Tl was primarily extracted in the residual fraction (1.31–78.7 mg/kg, 75.3–90.3%), followed by the reducible-(0.30–3.95 mg/kg, 4.53–17.2%), oxidizable- (0.06–3.53 mg/kg, 3.45–4.05%), weak acid soluble-(0.06–0.82 mg/kg, 0.94–3.45%), and water soluble- (0.01–0.14 mg/kg, 0.16–0.57%) fractions. In the pot trial soil, Tl was also mostly found in the residual fraction (6.47–11.5 mg/kg, 68.9–87.8%), followed by the reducible fraction (0.96–3.02 mg/kg, 9.24–25.1%). In S203 and pot trial soil, the percentage of oxidizable fraction was lower compared with other soil samples. The lower SOM value was also observed (Table 3), and reflected the likelihood that Tl in the oxidizable fraction was bound with SOM. A similar conclusion was obtained by Ospina-Alvarez et al. (2014).

Table 3
Physico-chemical properties of soils.

Samples	pH	SOM[a] (g/kg)	CEC[b] (cmol/kg)	K (%)	Ca (%)	Na (%)	Mg (%)	Fe (%)	Mn (%)
S102	5.1	101	21.3	1.58	0.68	0.66	0.20	4.08	0.03
S203	5.0	63.0	26.9	1.41	1.24	0.44	0.81	5.03	0.04
S204	5.8	146	20.1	1.03	0.59	0.74	0.38	4.75	0.07
Soil for pottrial	6.3	70.3	21.5	0.38	1.03	0.01	0.29	4.38	0.05

[a] SOM: soil organic matter.
[b] CEC: cation exchange capacity.

Before the growth of green cabbage, the soil contained approximately 25.7–30.9% Tl in the 'unstable' (i.e., water soluble, weak acid soluble, reducible and oxidizable) fraction, whereas that percentage drop to 12.2–18.0% after emergence of the plants. This further proved that the 'unstable' fraction of Tl is taken up preferentially by plants. In fact, the distribution of Tl partitioning in soils is a dynamic process (Gomez-Gonzalez et al., 2015; Vanek et al., 2015; Liu et al., 2016). In this study, the percentage of reducible fraction of Tl changed from 20.7–25.1% before vegetation to 12.2–18.0% after plantation, and indicated that this fraction was the main source of Tl, which eventually got converted to the bioavailable fraction (i.e., water soluble and weak acid soluble) and finally was accumulated by plants.

The results of the DTPA-extraction Tl speciation (Tables 4, 5) showed that Tl in rhizosphere soil solution mainly existed as Tl(I), which was consistent with previously thermodynamic predictions (Xiong, 2007). The percentage of Tl(III) increased slightly in 8 mg/kg Tl(III)-spiked pot soil solution after vegetation, which may be related to the fact that Tl(I) is readily accumulated by plants. However, the distribution of

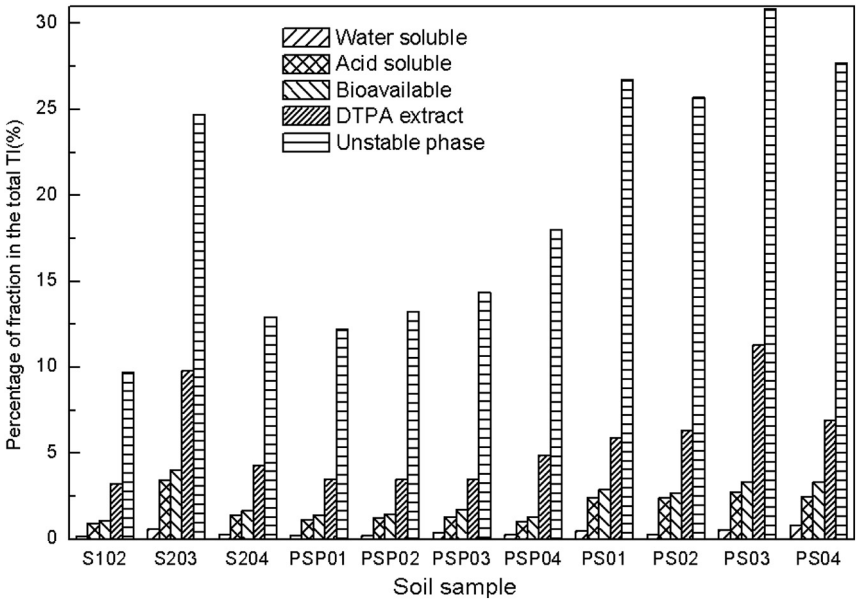

Fig. 3. Tl existing in various fractions in soils.

Table 4
The concentrations of total Tl and Tl in sequential extracted fractions in rhizospheric soils, and the percentage of Tl(I) and Tl(III) in DTPA-extracted soil solution.

Sample	Tl_{Total}	Tl in sequential fractions										Recovery[b] (%)	$Tl_{DTPA\ extracted}$			
		Water soluble		Acid soluble		Reducible		Oxidizable		Residual			(mg/kg)	Extraction rate[c]	Tl(I)	Tl(III)
	(mg/kg)	(mg/kg)	(%)[a]	(mg/kg)	(%)[a]	(mg/kg)	(%)[a]	(mg/kg)	(%)[a]	(mg/kg)	(%)[a]			(%)	(%)	(%)
S102(soil at mine area)	87.5	0.14	0.16	0.82	0.94	3.95	4.53	3.53	4.05	78.7	90.3	100	2.8	3.2	98.1	1.9
S203(alluvial soil)	1.50	0.01	0.57	0.06	3.45	0.30	17.2	0.06	3.45	1.31	75.3	116	0.15	9.8	99.1	0.9
S204(alluvial soil)	41.1	0.11	0.26	0.60	1.40	3.2	7.47	1.63	3.80	37.3	87.1	104	1.77	4.3	99.3	0.7
Pot trial soil	0.84															
PSP01(12 mg/kg Tl(I) + planted)	11.9	0.03	0.23	0.15	1.15	1.21	9.24	0.21	1.60	11.5	87.8	110	0.42	3.5	99.1	0.9
PSP02(8 mg/kg Tl(III) + planted)	8.95	0.02	0.21	0.12	1.26	0.96	10.1	0.16	1.68	8.26	86.9	106	0.31	3.5	96.4	3.6
PSP03(12 mg/kg Tl(I) + 3 g/kg Ca + planted)	9.62	0.04	0.4	0.13	1.29	1.10	10.9	0.18	1.78	8.67	85.8	105	0.33	3.5	99.1	0.9
PSP04(8 mg/kg Tl(III) + 3 g/kg Ca + planted)	7.23	0.02	0.25	0.08	1.01	1.15	14.6	0.17	2.15	6.47	82.0	109	0.35	4.9	96.7	3.3
PS01(12 mg/kg Tl(I) sipked)	13.9	0.07	0.49	0.34	2.39	3.02	21.3	0.36	2.54	10.4	73.2	102	0.81	5.9	99.5	0.5
PS02(8 mg/kg Tl(III) spiked)	10.1	0.03	0.27	0.27	2.41	2.32	20.7	0.26	2.32	8.30	74.1	111	0.63	6.3	99.2	0.8
PS03(12 mg/kg Tl(I) + 3 g/kg caspiked)	12.4	0.07	0.55	0.35	2.76	3.19	25.1	0.31	2.44	8.75	68.9	102	1.4	11.3	99.3	0.7
PS04(8 mg/kg Tl(III) + 3 g/kg caspiked)	9.50	0.08	0.83	0.24	2.49	2.15	22.3	0.20	2.07	7.02	72.8	102	0.65	6.9	99.2	0.8

[a] $[Tl_{Watersoluble\ or\ Weak\ acid\ soluble\ or\ Reducible\ or\ Reducible\ or\ Residual}/(Tl_{Watersoluble} + Tl_{Weak\ acid\ soluble} + Tl_{Reducible} + Tl_{Oxidizable} + Tl_{Residual})] * 100$.
[b] Recovery $= [(Tl_{Watersoluble} + Tl_{Weak\ acid\ soluble} + Tl_{Reducible} + Tl_{Oxidizable} + Tl_{Residual})/Tl_{Total}] * 100$.
[c] Extraction rate $= [Tl_{DTPA\ extracted}/Tl_{Total}] * 100$.

Table 5
Speciation and distribution of Tl in green cabbage.

Sample	Roots					Stems					Young leaves					Old leaves				
	Tl_{Total}	$Tl_{DTPA\ extracted}$				Tl_{Total}	$Tl_{DTPA\ extracted}$				Tl_{Total}	$Tl_{DTPA\ extracted}$				Tl_{Total}	$Tl_{DTPA\ extracted}$			
	(mg/kg)	(mg/kg)	Extraction rate[a]	Tl (I)	Tl (III)	(mg/kg)	(mg/kg)	Extraction rate[a]	Tl (I)	Tl (III)	(mg/kg)	(mg/kg)	Extraction rate[a]	Tl (I)	Tl (III)	(mg/kg)	(mg/kg)	Extraction rate[a]	Tl (I)	Tl (III)
			(%)	(%)	(%)			(%)	(%)	(%)			(%)	(%)	(%)			(%)	(%)	(%)
B102(plant frommine area)	33.2	31.2	94.0	95.0	5.0	38.1	39.4	103	93.7	6.3	658	630	95.7	96.3	3.7	1503	1489	99.1	98.2	1.8
B203(plants fromalluvial area)	2.10	2.00	95.2	96.2	3.8	2.80	2.60	92.9	96.5	3.5	5.30	5.10	96.2	94.2	5.8	37.9	36.0	95.0	99.3	0.7
B204(plants fromtalluvial area)	20.7	20.9	101	95.4	4.6	14.1	13.5	95.7	96.9	3.1	45.5	45.0	98.9	95.8	4.2	422	409	96.9	97.5	2.5
PB01(pot trial plants)	32.1	30.4	94.7	99.4	0.6	35.2	34.8	98.9	99.5	0.5	28.5	30.9	108	98.1	1.9	50.0	51.0	102	99.8	0.2
PB02(pottrial plants)	6.10	5.90	96.7	97.6	2.4	7.80	8.70	112	97.6	2.4	18.6	17.3	93.0	97.8	2.2	39.1	38.1	97.3	99.0	1.0
PB03(pot trial plants)	64.4	62.8	97.5	99.5	0.5	40.1	36.4	90.8	99.7	0.3	42.9	44.0	103	98.4	1.6	115	120	104	99.6	0.4
PB04(pot trial plants)	10.8	9.90	91.7	98.9	1.1	11.8	11.6	98.3	99.4	0.6	32.1	28.9	90.0	97.2	2.8	70.3	67.7	96.3	99.5	0.5

[a] Extraction rate $= [Tl_{DTPA\ extracted}/Tl_{Total}] * 100$.

DTPA-extracted Tl(I) and Tl(III) showed no significant difference between 8 mg/kg Tl(III) and 12 mg/kg Tl(I)-spiked pot soil. This indicated that after Tl(III) was added to the soil, most Tl(III) was reduced to Tl(I), and only little Tl(III) was stabilized by hydrolysis or colloid formation. There was no significant difference for Tl accumulation in plants between 12 mg/kgTl(I) and 8 mg/kg Tl(III)-spiked pot trials, which further confirmed the above explanation (Tables 4, 5). For green cabbage samples, Tl also mainly existed in the monovalent form Tl(I), especially in the old leaves where >97.5% of Tl was present as Tl(I). This finding is in line with previous studies (Nolan et al., 2004; Scheckel et al., 2004, 2007; Krasnodebska-Ostrega et al., 2008, 2012; Chu et al., 2012; Mazur et al., 2016).

Tl has two stable isotopes, ^{203}Tl and ^{205}Tl. Tl(III) is enriched in ^{205}Tl, isotope compositions higher than Tl(I) about 25–30 ε^{205}Tl ($\varepsilon^{205}\mathrm{Tl} = [(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_{\mathrm{NIST997}} - 1] * 10{,}000$) (Schauble, 2007). The transformation between Tl(I) and Tl(III) may cause significant isotopic fractionation. Kersten et al. (2014) revealed that significant Tl isotope fractionation of about −5 ε^{205}Tl between young leaves of green cabbage and the rhizospheric soil from the Lanmuchang Tl-polluted area in China, implying an enrichment of ^{203}Tl and Tl(I) in green cabbage samples. Previous studies have shown that Tl(III) would be stabilized in Mn-rich soils by incorporation into the Mn(IV)-oxide, or as Tl_2O_3 in soils contaminated with Tl(I)-bearing metal sulfides (Peacock and Moon, 2012; Nielsen et al., 2013; Voegelin et al., 2015). The Tl speciation analyses in the present study suggest that plants mainly take up Tl(I) from soil, and accumulate Tl(I) in plant tissues. This may indicate that Tl(III) would be reduced to Tl(I) in soils despite of an environment stimulating surface oxidation. The finding is interesting in the context of an increased understanding of the mechanisms of Tl isotope fractionation in the soil-plant system.

4. Conclusions

A method based on the use of microcolumns filled with immobilized oxine in the presence of DTPA was applied successfully to the separation and detection of Tl(I) and Tl(III) species in soil and plant samples. Results of Tl speciation analyses suggest that the fraction of Tl with the most environmental significance in soils consists of Tl(I). Tl in green cabbage crops, a hyperaccumulator plant, is also mainly present as Tl(I). With respect to Tl uptake in plants, this study provides direct evidence that green cabbage mainly takes up Tl(I) from soil. The finding is conducive to understanding the mechanisms of Tl isotope fractionation in the soil-plant system. Based on geochemical fraction studies, the reducible fraction was the main source of Tl accumulated by plant. In terms of methodology, the improved analytical method presented in this study offers an economical, simple, fast, sensitive method for the separation of Tl species at trace environmental concentrations.

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